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(54) DIAMOND IDENTIFICATION

(71) We, DE BEERS CONSOLIDATED MINES LIMITED, a Company registered under the laws of the Republic of South Africa, of 36, Stockdale Street, Kimberley, Republic of South Africa, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:–

This invention relates to the identification of diamonds, particularly diamonds of gem stone quality.

Diamonds of gem stone quality have of course been for many years of great value both for decorative and for investment purposes. The value of such diamonds has continued to increase, and this very increase in value had raised further problems for the police authorities and insurance companies. When a gem diamond is lost or is stolen, it can be difficult for the police authorities to identify a recovered diamond as being that which was stolen or lost especially since the nature of the diamond can be superficially changed by such techniques as re-polishing, re-cutting and irradiation.

The identification of a recovered diamond has in the past been performed by assembling a 'finger print' of the easily recognised features of the diamond. Such features include the carat weight, cut, clarity and colour of the diamond; others are the results of various physical tests performed on the diamond. The latter features include the measurement of surface irregularities using e.g. the Nomarski differential interference contrast, or techniques measuring bulk average properties e.g. fluorescence, magnetic, optical absorption and electron spin resonance measurements. However, although such a finger print of a diamond might be constant enough to enable the authorities to identify a particular diamond when it is recovered, this can only be done if the nature of the diamond has not been changed as mentioned above. Further, this finger printing technique can in general only be performed on cut diamonds; it is not suitable for rough diamonds. However, the security arrangements in diamond mines and in diamond cutting establishments do require that a check can be made at all times on the rough diamonds and then the partially cut and fully cut diamonds passing through the mine or cutting establishment. There is at present no technique available for identifying a particular cut diamond from the rough stone from which it has been cut; clearly there is a need for such a method.

It has now been found that the application of topography can provide a finger print of a diamond, both in the rough as well as the cut state, which finger print is not changed if the diamond is subjected to re-polishing, re-cutting and/or mild irradiation. The finger print is only changed if the characteristic crystalline nature of the diamond is profoundly changed by converting it, for example, to amorphous carbon. Topography is a technique which depicts point-by-point throughout its whole volume certain properties of a specimen. Thus topographical studies are of particular value whenever the inhomogeneity of the specimen is of interest (see e.g. Lang, 'Modern Diffraction and Imaging Techniques in Material Science', North-Holland Publishing Co., Amsterdam-London, 407 (1970)).

The present invention provides a set of records of internal defects of a diamond, the records having been produced by X-ray topography using either:–

(a) monochromatic X-radiation reflected at the Bragg angle from crystallographically equivalent planes of the diamond lattice structure, Bragg reflections from each such plane being recorded from a plurality of directions of view, or

(b) white X-radiation incident upon the diamond in directions having a constant angular relationship to each equivalent axis of symmetry of the diamond lattice structure, Bragg reflections being recorded for each said direction of the incident X-radiation,

in either case, the set being such as to pro-

vide an overall point-by-point three-dimensional representation of the diamond, as well as a collection of said sets, the sets having been produced using the same directions and, in the case of sets produced using monochromatic X-radiation, the same crystallographically equivalent planes. The present invention also provides a method of determining whether a diamond is the same as or different from a known diamond which comprises producing by X-ray topography a set of records thereof similar to those of a collection of this invention, so as to provide an overall point-by-point three-dimensional representation of the internal defects thereof, and comparing the set so produced with records of a set in the collection as well as a method of determining whether a diamond is the same as a specific diamond which comprises maintaining a set of records of this invention of internal defects of the diamond, making a similar set of records of the unidentified diamond and comparing that set with the maintained set.

As one skilled in the art will appreciate the expression 'crystallographically equivalent' planes means, to take the faces of a cube as a simple example, the planes denoted by {100} viz. (100), (010) and (001) (and ($\bar{1}00$), ($0\bar{1}0$) and ($00\bar{1}$)). It is not, of course, sufficient to use parallel planes which would not normally be regarded as 'crystallographically equivalent' since this would not enable one to obtain an overall record of the diamond in question. Using these cube planes it would be necessary to obtain reflections from each independent plane, in this example the three planes (100), (010) and (001), in order to obtain the three-dimensional overall view.

In the methods of this invention a set is considered to be 'similar' if it has been obtained using the same directions, and, in the case of sets produced using monochromatic X-radiation, the same crystallographically equivalent planes, as were used for the original set(s). By the term 'Bragg angle' is meant the angle which satisfies the equation known as Bragg's Law:–

$$2d_{hkl} \sin \theta = n\lambda$$

In this equation, d_{hkl} is the interplanar spacing of those crystal lattice planes whose orientation in the crystal lattice is denoted by the index hkl, the angle θ is the angle made by the beam of X-rays with the above-mentioned planes, n is an integer and λ is the wavelength of the X-rays concerned. X-ray diffraction radiographs (also known as X-ray diffraction topographs) taken at the Bragg angle show characteristic patterns, which are of such a nature that it is unlikely that more than one diamond will possess exactly the same finger print, particularly if a series of X-ray diffraction radiographs are taken in the various planes but still using the Bragg reflection angle. It is to be understood that the expression 'using X-ray diffraction at the Bragg Angle' is employed herein in the general sense. If the specimen contains some regions of the crystal which are significantly mis-oriented with respect to other regions in the crystal then, when the wavelengths contained in the X-ray beam incident upon the crystal are restricted to a sufficiently narrow range, and there is a sufficiently small angular divergence of the X-ray beam incident upon the specimen, some crystal regions may satisfy Bragg's Law whereas others may in effect fail to do so, at a given angular setting of the crystal with respect to the mean orientation of the incident X-ray beam. Such a mis-orientation in the specimen can be recorded, and may in fact be included as comprising part of the X-ray topographic record of internal defects in the diamond. In other words it is possible to illuminate the specimen with an X-ray beam whose spectral distribution and whose range of orientations with respect to the specimen (or said selected region) are so chosen that a fraction of the specimen (or of said selected region) departs from exact satisfaction of the condition of X-ray diffraction at the Bragg angle by a determined small angle. The sensitivity of contrast, nature of contrast (i.e. excess or deficiency of diffracted intensity) and the range of contrast with which these mis-orientations (and also lesser mis-orientations such as are associated with individual crystal lattice dislocations) are recorded depend upon the degree of collimation and wavelength spread of the X-rays incident upon the specimen. Thus the contrast characteristics of the X-ray topographs will in general depend upon whether the X-radiation incident upon the specimen is collimated by slits, or is collimated and/or monochromatized by prior Bragg reflection by a so called 'monochromator' crystal, and also upon whether the origin of the radiation is a conventional X-ray generator or is a synchrotron source. It is to be understood that such practical variations and subtleties are included within the terms 'using X-ray diffraction at the Bragg angle' and 'satisfying Bragg's Law', as used herein.

In the method of the invention there can be used the Bragg reflection from crystal lattice planes differing in orientation and, if desired, interplanar spacing by means of projection and/or section topography according to a predetermined routine designed to maximise the information content regarding the internal distinguishing features of the crystal. The use of this X-ray topographic technique makes it possible to identify crystal lattice imperfections e.g. crystal lattice dislocations in the diamond, growth bands, stacking faults and twinning.

As will be seen from the Bragg's Law equation, if the X-radiation is monochromatic (or nearly so) then the crystal must be set at such an angle with respect to the range of directions of rays contained within the incident X-ray beam that the Bragg's Law equation is satisfied for at least one crystal lattice plane (hkl). In this case the X-ray topographs will be recorded serially.

On the other hand, if the X-radiation is not monochromatic, and the so called 'white radiation' emitted by an X-ray tube, or the X-rays produced by a synchrotron, is used, then, at each angular setting of the crystal with respect to the incident beam, a group of Bragg reflections, each arising from a differently oriented crystal lattice plane, may be simultaneously recorded as in the technique described by Guinier and Tennevin, Acta Crystallographica, 1949, 2, 133-8. It is a matter of choice, depending much upon the characteristics of the X-ray source available, whether Bragg reflections are recorded serially (making use of X-rays of a given wavelength) or simultaneously in groups as in the technique of Guinier and Tennevin cited above. If the latter technique is used, then it would be advantageous to record groups of reflections when a symmetry axis is oriented parallel to the axis of the incident X-ray beam. For example, groups of reflections could be recorded with, for each group, one of the three cubic symmetry axes oriented parallel to the beam i.e. in this case, the angular relationship to each equivalent axis of symmetry is such that the angle is 0.

A series of diffraction radiographs using crystallographically equivalent reflections is taken. The simplest routine, when using monochromatic radiation, is to select the three cube planes in which four radiographs are taken in each plane; between the taking of each radiograph, the crystal is rotated 90° round the perpendicular to the plane to give an overall picture for the stone. Thus it will be appreciated that when using monochromatic X-radiation in order to obtain an overall three-dimensional picture which is reproducible it is necessary, to make more than one record, using different directions of view, for each equivalent plane. In contrast using white X-radiation it is possible to record different directions of view on a single record.

In order to obtain an overall three-dimensional view it will be appreciated that it is necessary to obtain at least three records, this being the case where a record is taken at each of three mutually perpendicular axes or planes of symmetry.

The radiograph can be registered in permanent or semi-permanent form by the usual techniques, e.g. by X-ray 'Polaroid' (Registered Trade Mark) techniques, X-ray sensitive photographic emulsions, xerography and electronic techniques; such electronic techniques include electronic image intensifiers (with or without television apparatus added thereto) and position-sensitive gas-filled or solid-state X-ray photon detectors (used singly, or multiply in an array). The records may, for example, be in the form of magnetic tapes. The source of the X-rays (which should be collimated) can be either from a conventional X-ray tube or from a synchrotron, the synchrotron being a source of highly collimated and highly intense X-rays.

It is possible to distinguish between synthetic and natural diamonds by this topographic technique, in general because the synthetic diamonds currently available possess types of inclusion, due, for example, to metallic impurities, which are not present in natural diamonds.

Some diamonds e.g. rough diamonds, particularly those from an alluvial source have surface damage and it is desirable to remove as much of the surface damage as possible prior to producing the X-ray topograph record or records of the diamond. Removal of surface damage enables the internal distinguishing features of the diamond to be revealed with improved clarity and contrast in the X-ray topographs. Surface damage may be removed by etching using for example a gas at controlled temperatures and pressures, reactive gases in the presence of electric currents, agitated liquids and high velocity ions and atoms.

Where a rough diamond has a coating thereon, the X-ray topograph or topographs can indicate whether the stone is worth the expense and effort of opening it.

It is believed that the insurance companies and police authorities will build up an index of X-ray topographs of known diamonds to collections of X-ray topographs according to our invention. For example the index may comprise an abstract, summary or codification descriptive of the configurations of one or more types of internal defects, such as stacking faults, twins, slip bands and small-angle grain boundaries (misorientations) and, especially, lattice dislocations, growth horizons or bands and strain fields associated with submicroscopic inclusions or precipitates, as recorded by X-ray topography.

To illustrate the nature of X-ray topography the accompanying radiographs (Figures 1 and 2) show X-ray diffraction pictures of a one carat brilliant diamond. Figure 2 is a projection topograph (Lang, Acta Crystallographica, 1959, 12, 249-250), while Figure 2, which is roughly elliptical in shape, is an X-ray section topograph (this technique is discussed by Lang, Acta Metallurgica, 1957, 5, 358-364) cutting through the brilliant diamond roughly parallel to its widest section parallel to the table, i.e. a section parallel to the girdle. The section topograph shows very sharp detail and hence a high degree of uniqueness, but it represents just one cut through the crystal. The projection topograph shows a reflection of the whole volume of the crystal and so is somewhat less sharp. This particular diamond is rather pathological from the crystal growth point of view (but, apparently, having an internal structure not very uncommon). Hence it was not an easy subject for finger printing since it contained so much imperfection. Such pictures, together with some more of the same stone, would constitute a unique and unambiguous finger print, unalterable by any method that would not also ruin the stone itself.

In an Example of the invention, X-ray diffraction topographs of three rough diamonds,

FIG. 1

FIG. 2

FIG. 3

FIG. 4